

Furnace Injection of Alkaline Sorbents for Sulfuric Acid Control

Gary Blythe and Richard McMillan
URS Corporation
P.O. Box 201088
Austin, Texas 78720

Jake Davis and Mark Lamison
First Energy Corporation
P.O. Box 128
Shippingport, Pennsylvania 15077

Richard Rhudy
EPRI
3412 Hillview Avenue
Palo Alto, California 94304

Joel Beeghly, Lew Benson and Ed Goetz
Carmeuse NA
3600 Neville Road
Pittsburgh, PA 15225

ABSTRACT

This project is testing the effectiveness of alkaline reagents injected into the furnace of coal-fired boilers at controlling sulfuric acid emissions. Sulfuric acid is present in most coal combustion flue gases because a small percentage of the SO_2 produced (approximately 0.5 to 1.5%) is further oxidized to SO_3 , which combines with flue gas moisture to form vapor-phase or condensed sulfuric acid. Sulfuric acid is a Toxic Release Inventory substance and a potential precursor to acid aerosol/condensable emissions from coal-fired boilers, and can lead to air heater corrosion, plugging and fouling, and a visible plume at some plants. These effects will likely be exacerbated if selective catalytic reduction (SCR) is retrofitted for NO_x control, as SCR catalysts are known to further oxidize a portion of the flue gas SO_2 to SO_3 .

The project is co-funded by the U.S. Department of Energy's National Energy Technology Laboratory (DOE/NETL), EPRI, First Energy Corporation, the Tennessee Valley Authority (TVA), and Carmeuse NA (was Dravo Lime Company). The project has tested the effectiveness of each of four calcium- and/or magnesium-based sorbents in one- to two-week furnace injection tests conducted at First Energy's Bruce Mansfield Plant (BMP). One sorbent was produced as a flue gas desulfurization (FGD) system byproduct, while the other three are commercially available alkalis. The four short-term tests have been completed, and the first of two longer-term (up to 30-day) tests with the most promising sorbent is underway. The second longer-term test will be conducted later on a TVA unit. The longer-term tests are to confirm the effectiveness of

the sorbent(s) over extended operation, and to determine balance of plant impacts. Results from the short-term tests are presented and discussed in the paper.

INTRODUCTION

The objective of this project is to demonstrate the use of alkaline reagents injected into the furnace of coal-fired boilers as a means of controlling sulfuric acid emissions. The coincident removal of hydrochloric acid and hydrofluoric acid will also be determined, as will the removal of arsenic, a known poison for SCR catalysts. URS Corporation (formerly Radian International) is the prime contractor. The project is being funded by DOE/NETL Cooperative Agreement DE-FC26-99FT40718. EPRI, TVA, First Energy, and Carmeuse NA are co-funders.

Sulfuric acid is present in most flue gases from coal combustion because a small percentage of the SO_2 produced from the sulfur in the coal (approximately 0.5% to 1.5%) is further oxidized to form SO_3 . The SO_3 combines with flue gas moisture to form vapor-phase or condensed sulfuric acid at temperatures below 500°F. Besides being a Toxic Release Inventory substance and a potential precursor to acid aerosol/condensable emissions from coal-fired boilers, sulfuric acid in the flue gas can lead to boiler air heater plugging and fouling, corrosion in the air heater and downstream, and the formation of a visible plume. These issues will likely be exacerbated with the retrofit of SCR for NO_x control on some coal-fired plants, as SCR catalysts are known to further oxidize a portion of the flue gas SO_2 to SO_3 .

The project has tested the effectiveness of furnace injection of four different calcium- and/or magnesium-based alkaline sorbents on full-scale utility boilers. The reagents were tested during four one- to two-week tests conducted on a First Energy BMP unit. One of the sorbents was produced as a wet FGD system byproduct, and the other three are commercially available in quantity.

After completing the four one- to two-week tests, the FGD byproduct was selected for longer-term (up to 30-day) full-scale tests. The longer-term tests will be used to confirm the effectiveness of the sorbents tested over extended operation, and to determine balance-of-plant impacts. Two longer-term tests will be conducted, one on First Energy's BMP Unit 3 and the second is planned for a TVA unit. At the completion of the project, it is expected that sufficient full-scale test data will be available to design and implement commercial installations of the sulfuric acid control technologies tested.

TECHNICAL APPROACH

Four short-term sorbent injection tests have been conducted at BMP to investigate the effectiveness of alkaline sorbents for sulfuric acid control, and evaluate effects of these sorbents on boiler equipment performance. The first short-term test investigated the effect of injecting dry dolomite powder ($\text{CaCO}_3 \bullet \text{MgCO}_3$), into the furnace of Unit 2 for a period of four days. The other three short-term (approximately two-week) tests involved sorbent slurry injection in the furnace of BMP Unit 3. The three slurry injection tests evaluated pressure-hydrated dolomitic lime [$\text{Ca}(\text{OH})_2 \bullet \text{Mg}(\text{OH})_2$] (PHDL), commercially available magnesium hydroxide [$\text{Mg}(\text{OH})_2$] (commercial Mg) and a byproduct magnesium hydroxide (byproduct Mg) for SO_3 control.

During these tests, various analytical techniques were used to quantify the effectiveness of sorbent injection. First, sampling was conducted by the controlled condensation system (CCS) method for determining the SO_3 content of the flue gas. EPA Method 26a was used to determine hydrochloric acid (HCl) and hydrofluoric acid (HF) concentrations in the flue gas. Fly ash resistivity was measured using a Wahlco resistivity probe, and unburned carbon in fly ash was determined by loss on ignition (LOI). Coal samples were also collected and analyzed for a variety of parameters. Finally, visual observations were made of boiler furnace and convective pass surfaces prior to and during sorbent injection.

Unit 2 at BMP is rated at 780 net MW, and Unit 3 is rated at 800 net MW. Each has an opposed-wall fired, supercritical boiler with 16 burners each on the front and back walls of the furnace. On both units, the burners are arranged in four horizontal rows on each wall, with four burners per row. One ball mill pulverizer provides the pulverized fuel for each row. Depending on fuel quality and mill condition, full load can generally be achieved with six of the eight mills in operation (and thus six of eight rows of burners in service). Both units burn a bituminous coal blend typically containing 4% sulfur. The facility also has permission to burn up to 20% of the fuel as petroleum coke. During test periods a standard coal blend (i.e., no petroleum coke co-firing) was typically fired, although for a portion of the byproduct Mg test a small amount of petroleum coke was reportedly blended with a lower sulfur coal.

Figure 1 illustrates the flue gas path for Unit 2, and notes the gas sampling locations during the dolomite injection test. The boiler has two air heaters following the economizer section. The average flue gas temperature at the air heater outlet is controlled to about 300°F due to acid dew point considerations. Flue gas from the two air heaters goes to a common plenum, then to six venturi scrubbers that remove particulate material and SO_2 . The scrubbers use magnesium-enhanced, Thiosorbic[®] lime slurry reagent and produce calcium sulfite hemihydrate ($\text{CaSO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$) byproduct. The flue gas then passes through induced draft (ID) fans, one per scrubber module. The six scrubbed flue gas streams are combined in two ducts that each lead to separate flues in the stack. The flue gas from Units 1 and 2 is combined in one stack. The flue gas in the stack is saturated at a temperature of about 130°F; no reheat is employed.

During the dolomite injection tests, the top rows of burners on the front and rear walls of the unit were generally out of service. Injection of dolomite was through the top row of burners on the front wall. This was accomplished by charging the coal storage hoppers that feed these burners with dolomite, which was then fed to the pulverizer and blown through the burners into the furnace.

During the other three tests, alkaline sorbent slurries were injected into one half of the Unit 3 boiler for up to two weeks each, to assess their effectiveness for flue gas SO_3 control. Most analytical techniques employed were similar to those used during dolomite injection on Unit 2. In addition, impacts on electrostatic precipitator (ESP) operation were quantified by taking voltage and current data on electrical sections of the Unit 3 ESP's. Also, sorbent and ESP hopper samples were analyzed for magnesium content, and sorbent samples were analyzed for density, weight percent solids, and total alkalinity.

Figure 1: Illustration of the flue gas path for BMP Unit 2

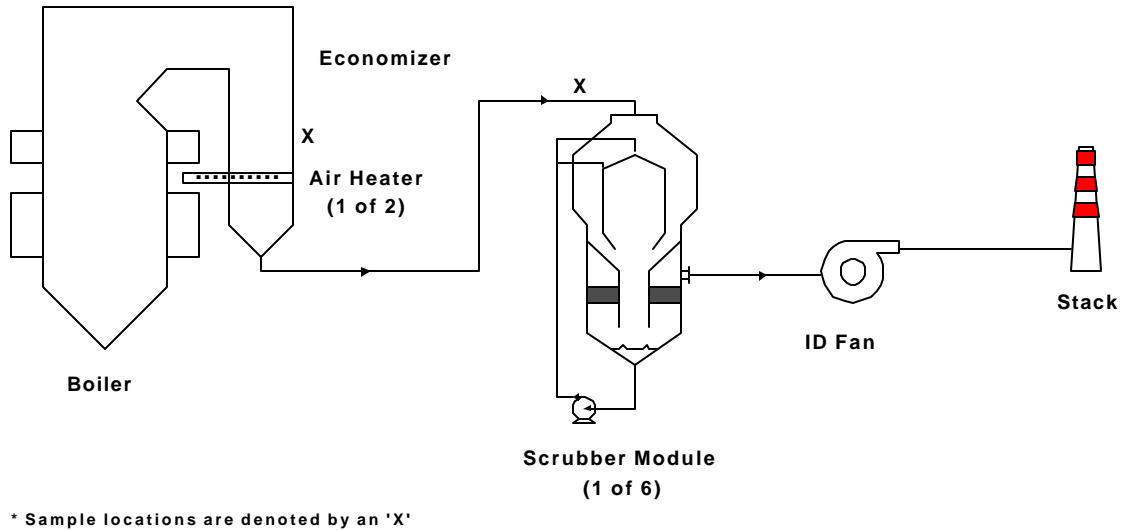
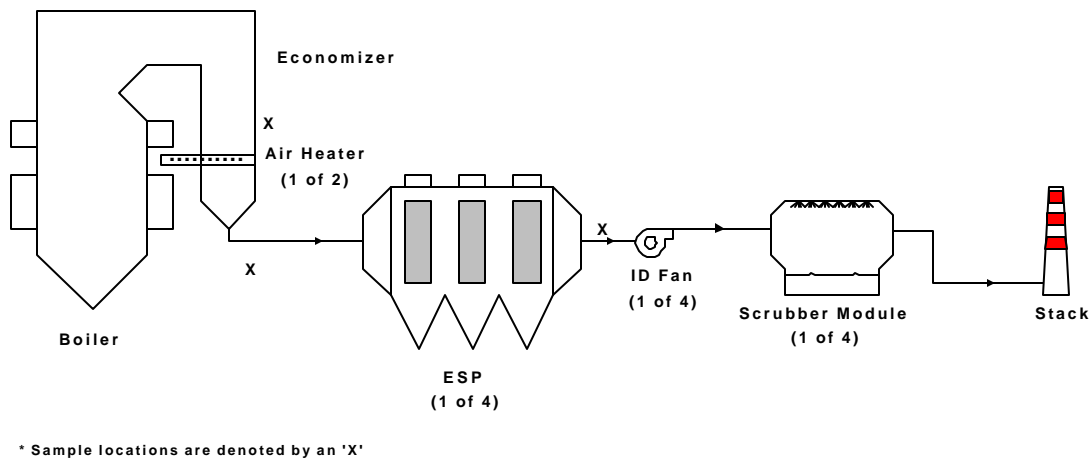


Figure 2 illustrates the flue gas path for Unit 3, and notes the gas sampling locations used during this test. Flue gas from each of the two air heaters splits into two duct runs, each of which goes to an ESP followed by an ID fan. There are no ties between the four ducts (two per air heater), so when an ID fan is out of service there is no gas flow through the associated air heater outlet duct and ESP. Correspondingly, the gas flow through that air heater is also reduced. Downstream of the ID fans, the flue gas flows to a common plenum, then splits to five horizontal-gas-flow FGD absorber modules (four normally operate at full load). The scrubbers use magnesium-enhanced, Thiosorbic[®] lime slurry reagent and produce calcium sulfite hemihydrate byproduct. The flue gas, which is saturated at a temperature of about 130°F, then goes to a dedicated stack for Unit 3.

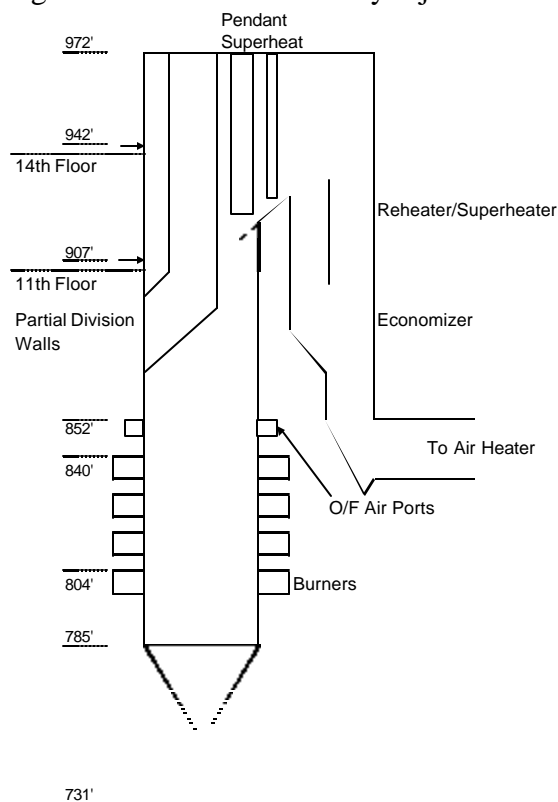
Figure 2: Illustration of the flue gas path for BMP Unit 3



Sorbent slurries were injected through up to six air-atomizing nozzles inserted into one-half of the front wall of the boiler. During the PHDL and commercial Mg test, the slurry was fed through ports at the 11th floor of the boiler structure, across from the “nose” of the boiler. Midway through the byproduct Mg test, the injection location was elevated to the 14th floor, across from the

pendant superheat platens. The injection levels are indicated by arrows in Figure 3. At either level, the slurry injection lances were inserted through existing furnace inspection ports. At both levels there are twelve ports across the face of the boiler. There is a port adjacent to each corner of the front wall, and the remaining ports are situated on either side of five partial division walls that are equally spaced across the upper furnace. Figure 4 illustrates the six lance locations on the east half of the boiler. For the 14th floor injection, location No. 5 was blocked by a camera installed at that inspection port, so the slurry flow was split among five nozzles instead of six.

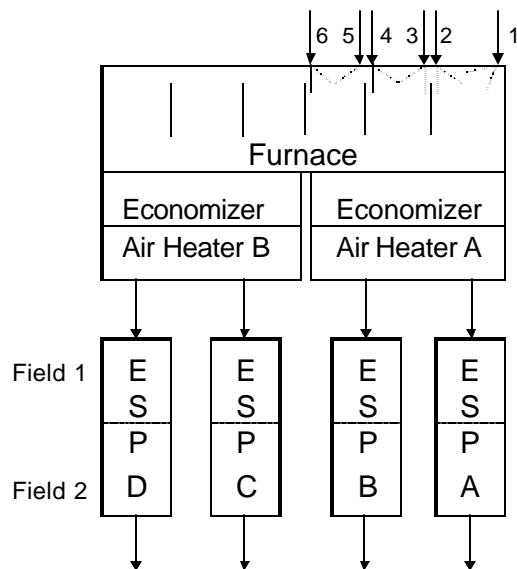
Figure 3: Illustration of slurry injection levels



The air-atomizing nozzles were designed by Ashworth Engineering specifically for this application. The proprietary design employs an internal mix configuration, and was designed for relatively low airflow requirements and to achieve a relatively large minimum passage diameter. The air pressure to the nozzles was typically 80 psig.

The sorbents were delivered to the site in truckload quantities, as slurries containing 15 to 60 wt% solids depending on the reagent. The tanker trucks unloaded into two 10,000-gallon storage tanks situated in the basement of Unit 3. One of two air-driven diaphragm pumps was used to transfer slurry from the storage tanks to a 1000-gallon “day” tank on the 9th floor of the boiler structure. From the day tank, one or two Moyno progressing cavity pumps were used to feed slurry to the injection nozzles. There is a flow meter at the outlet of each pump. Pump speed was modulated to maintain slurry flow rate, which was adjusted according to the density and purity of the reagent, the Unit 3 load and estimated coal sulfur content, and the desired reagent-to-SO₃ molar ratio. The

Figure 4: Illustration of slurry injection locations – plan view



Moyno pumps fed a manifold that distributed slurry to the five or six injection nozzles. Plant compressed air was connected to each lance individually, through flexible hoses.

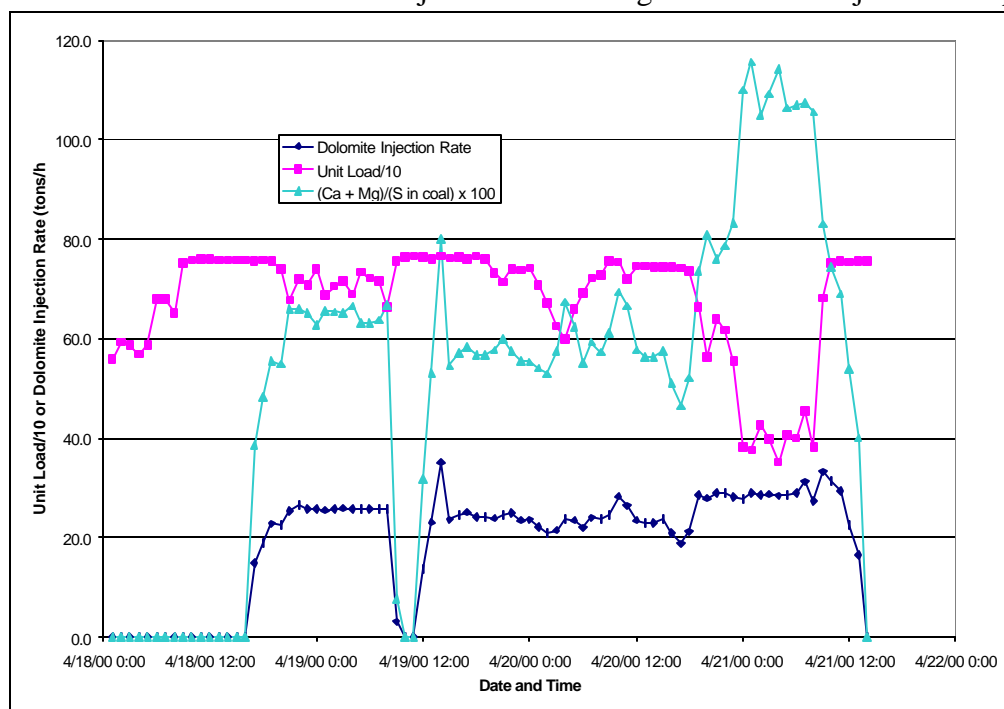
Figure 4 also illustrates the arrangement of the four ESP's relative to the two air heaters. Because of the rotation of the regenerative air heaters, flue gas going to the outboard ESP's (labeled "A" and "D" in Figure 4) tends to be cooler and have a lower SO₃ content than the flue gas going to the inboard ESP's (labeled "B" and "C"). However, no attempt was made to bias slurry flow to the nozzles on the inboard side of the air heater to account for the stratification. It was felt that the stratification was caused by the gas temperature drop across the air heater, and not reflective of stratification in furnace gas SO₃ content where the sorbent was injected.

RESULTS OF DOLOMITE INJECTION TEST ON UNIT 2

Dolomite was injected April 18 through April 21, 2000. Flue gas characterization tests were only conducted during daylight hours. During the day the unit was close to full load with two burner rows out of service (typically the top row on the front and rear walls). Overnight the boiler load was reduced, but dolomite injection rates were maintained relatively constant due to minimum flow requirements on the mill used to grind the dolomite. Figure 5 illustrates boiler load and dolomite injection rates during the test.

Also shown in the figure is the molar ratio of alkalinity in the dolomite injected to sulfur in the coal fired. This molar ratio is proportional to the ratio of dolomite alkalinity to sulfuric acid in the flue gas. For the figure, the alkalinity in the dolomite includes both calcium carbonate and magnesium carbonate content, and the coal sulfur is based on the measured coal feed rates and average coal sulfur analyses. Coal sample ultimate and proximate analyses showed an average of 4.1% sulfur and an average coal HHV of about 12,000 Btu/lb during the test.

Figure 5: Boiler load and dolomite injection rate during the dolomite injection test period



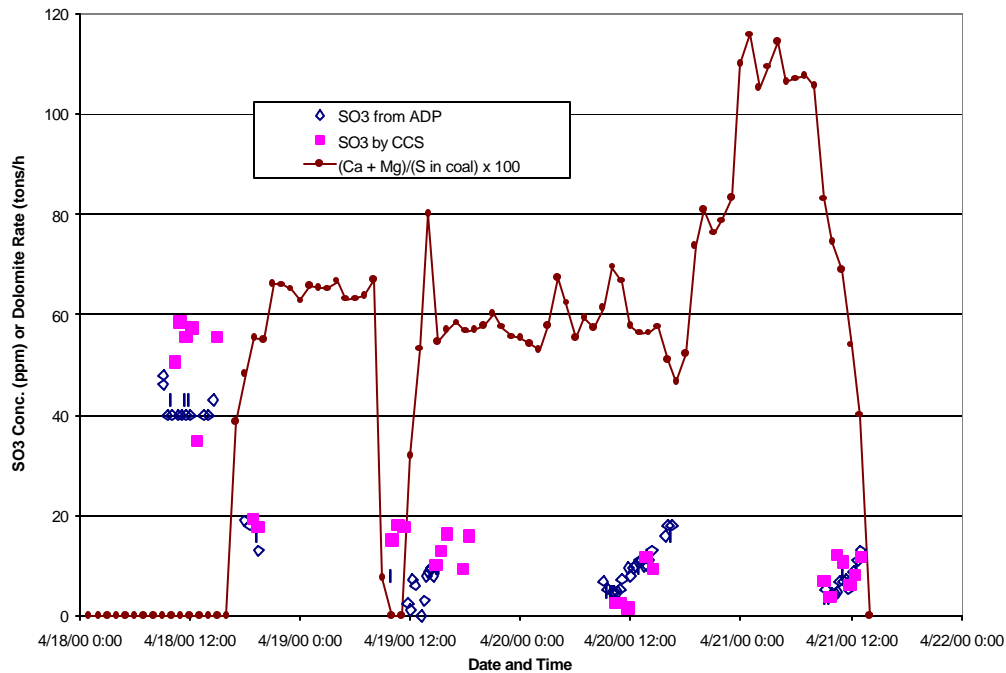
SO₃/Sulfuric Acid Measurements

SO₃ measurements were made by the CCS method at the economizer exit in the east duct. Acid dew-point (ADP) measurements were made with a Land Combustion monitor at the air heater outlet. Figure 6 plots the CCS and ADP data during the week. The results indicate a significant reduction in flue gas SO₃ concentration and acid dew point as soon as dolomite injection began.

The flue gas SO₃ concentration dropped by over 60%, from approximately 52 ppm to 19 ppm within two hours. The SO₃ data show a continued downward trend over the first two days of dolomite injection. On the second day of testing, dolomite injection was interrupted for several hours. Despite the interruption, flue gas SO₃ levels remained relatively low (15 ppm to 18 ppm), indicating a residual effect of previously injected dolomite. Over the last two test days, the measured SO₃ concentrations averaged 7 ppm and ranged from 2 to 12 ppm. Relative to the pre-injection average of 52 ppm, this indicates an average of 86% reduction in economizer outlet SO₃ concentration. Over this period, the dolomite injection rate averaged 25.7 tons/hr, which represents about 8.8% of the coal feed rate. The alkalinity in the dolomite (calcium plus magnesium) represents about a 0.7:1 mole ratio compared to the sulfur in the coal, and about a 40:1 mole ratio compared to the amount of SO₃ produced under baseline conditions (about 1.7% of the coal sulfur was oxidized to SO₃). During the periods when SO₃ concentrations were actually measured, though, the dolomite molar ratio to coal sulfur was slightly lower, at about 0.62:1, due to higher unit load during the day. Dolomite injection had little effect on the concentrations of two other acid gases in the flue gas; no removal of HCl or HF was measured.

The dolomite feed rate was adjusted several times during the week in an attempt to establish SO₃ removal as a function of feed rate. During these short-term variations, there was a clear response

Figure 6: CCS SO₃ measurement data for the dolomite injection test



of SO₃ concentrations to changes in dolomite feed rate, with increased feed rates resulting in lower SO₃ values and vice versa. However, in most instances the feed rate changes were too rapid to establish an SO₃ concentration that could be considered representative for a given dolomite feed rate.

There were two periods where the injection rate was held relatively constant for several hours, so the CCS data may be representative of the particular dolomite rate. Late on April 19 the injection rate averaged 24.4 tons/hr, and CCS data averaged 14 ppm of SO₃. This indicates an average removal of about 74% at a molar ratio of dolomite injected to coal sulfur of 0.57:1. The morning of April 20 the dolomite injection rate averaged 27.4 tons/hr over a two-hour period. CCS runs averaged 2.6 ppm of SO₃, indicating about 95% SO₃ removal relative to baseline, at a molar ratio of dolomite injected to coal sulfur of about 0.68:1. More time at a particular unit injection rate and unit load would be preferable, though, to provide more confidence in the SO₃ removal values.

Balance of Plant Effects

One concern about dolomite injection was the potential for increased slagging in the upper furnace. A moderate increase was observed. Prior to injection, the upper furnace side walls, partial division walls and pendants had very little slag accumulations, with ½ to 1 inch of slag build-up. After three days of injecting dolomite, the slag accumulations on the side wall varied from 0 to 2 inches thickness, accumulations on the partial division walls were between 1 and 2 inches and the pendant superheaters had between 2 and 4 inches of slag accumulation. There did not appear to be any bridging of flue gas flow passages. Dolomite injection appeared to have an adverse effect on unit heat rate, as the average air heater exit temperature at a load of 760 gross MW was observed to increase by 8°F over the duration of the test.

Because Unit 2 does not have an ESP for particulate control, the entrained, partially utilized dolomite was removed from the flue gas in the wet-lime FGD scrubbers. Chemical analyses of the scrubber solids indicate that virtually all of the calcium content and about half of the magnesium content in the dolomite was used to react with SO_2 removed in the scrubbers. Between the two components, about half of the normal FGD system lime slurry makeup was replaced by injected dolomite. The contribution from the magnesium content was due to magnesium dissolving into the liquid phase of the scrubber slurry. With time, as FGD liquor magnesium concentrations increase because of magnesium dissolving from the dolomite, solubility limits may begin to reduce the amount of magnesium in the dolomite available in the scrubber.

A potentially adverse effect of injected dolomite on the FGD system was that magnesium oxide not utilized in the scrubber might continue to hydrate and dissolve in the thickener, to the point where magnesium sulfite could precipitate there. Although the pH of the thickener underflow and overflow did increase above scrubber pH values, indicating further magnesium oxide hydration in the thickener, no magnesium sulfite precipitation was observed. This could become an issue as the liquor magnesium concentration cycles up, though. Another concern was about the potential for gypsum scaling in the scrubbers. Analyses of the recycle liquor did not indicate increased gypsum scaling potential during dolomite injection. However, it remains possible for scaling at localized areas of the scrubber, such as around the wet/dry interface.

Overall, dolomite injection into the furnace appeared to be effective at lowering flue gas sulfuric acid concentrations by up to 95%, and particularly suited to Unit 2 where the dolomite injected offsets the consumption of lime reagent in the FGD system. As described above, though, there are a few technical uncertainties that require additional testing to resolve.

RESULTS OF SLURRY INJECTION TESTS ON UNIT 3

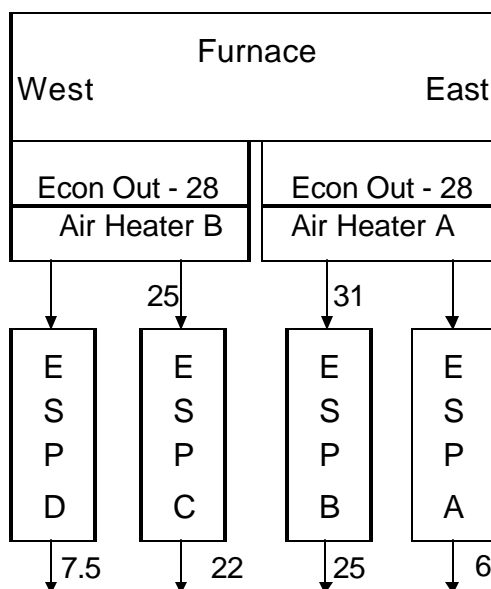
Testing was conducted on Unit 3 during four discrete time periods, including baseline (no sorbent injection), PHDL testing, commercial Mg testing, and byproduct Mg testing. Flue gas SO_3 concentrations determined by the CCS method were the primary measure of sorbent performance. Flue gas characterization tests were typically conducted during daytime hours each test day, although there were periods during the PHDL and commercial Mg tests where sampling was conducted between 1:00 a.m. and 5:00 a.m. Such early morning tests were conducted because overnight the unit was at low load, which allowed higher sorbent-to- SO_3 mole ratios than could be achieved at full load, and lowered furnace temperatures at the point of sorbent injection. These effects are discussed further below.

During the day, the unit operated close to full load with one to two pulverizers and burner rows out of service. Average daytime loads were typically in the range of 800 gross MW \pm 50 MW. One exception was during the first week of the byproduct Mg test, when coal quality and slagging concerns limited the unit load to around 700 MW \pm 50 MW. In most cases overnight loads were reduced into the range of 550 to 650 gross MW, although the load sometimes remained above 700 MW due to grid demand. The sorbent injection rate was typically reduced overnight in proportion to unit load, except during the early morning flue gas testing periods, when the maximum sorbent injection rates were maintained to allow operation at high sorbent-to- SO_3 mole ratios.

Baseline Results

The primary objectives of the baseline measurements conducted in early October was to measure SO_3 concentrations with no sorbent injection, at a variety of measurement locations. Figure 7 summarizes the results of the baseline CCS measurements, showing the average of all measurements made at a particular location during the week.

Figure 7: Summary of baseline CCS measurements at BMP Unit 3



When presented as averages in Figure 7, the results show no significant side-to-side variation in SO_3 conversion in the furnace and back pass of the boiler, and little or no SO_3 removal across the “hot” sides of the air heaters (11% or less). SO_3 does not appear to be removed across the “B” and “C” ESP’s at a high percentage either; on average the removal percentage across these two ESP’s varies from 11 to 20%. The sampling ports for the outlet of the “cold” side of the air heaters and inlets to the “A” and “D” ESP’s are difficult to access on Unit 3, therefore no CCS measurements were made at those locations. However, comparing the economizer outlet values to the outlets of the “A” and “D” ESP’s, a total of 73% to 79% reduction in SO_3 concentration is seen. Most of this reduction is presumed to occur across the air heater. Because of the observed stratification of SO_3 concentrations between the ESP’s, it was decided to conduct most of the CCS measurements during sorbent injection tests on the “B” or “C” ESP inlet and outlet, where most of the flue gas SO_3 content is seen.

The economizer outlet SO_3 concentration data presented in Figure 7 were used to calculate an average SO_2 to SO_3 conversion percentage for Unit 3 to serve as a basis for setting sorbent injection rates and for reporting sorbent-to- SO_3 molar ratios. Ultimate analyses of Unit 3 coal feed samples for the baseline test show an average sulfur content of 4.1%. Using this coal sulfur content and the economizer outlet SO_3 concentrations measured, the average SO_2 to SO_3 conversion for Unit 3 was estimated at nominally 1%.

PHDL Test

The PHDL slurry tests were conducted the last two weeks in October 2000. The PHDL slurry is prepared by Clear₂O Technologies, who purchases PHDL powder from Gen Lime in central Ohio and prepares it as a 60-wt % aqueous slurry. The 60-wt % slurry proved to be more viscous than the slurry injection equipment could handle, so for this test Clear₂O produced a more dilute slurry at 35 wt %. This material was injected as a slurry rather than as a powder primarily because the other sorbents tested were available only as slurries, so testing the PHDL as a slurry allowed the same equipment to be used. The PHDL slurry solids were measured to have a mass mean particle diameter of 7 to 8 microns, and a specific surface area (by BET analysis) of 19 m²/g.

The calcium plus magnesium alkali-to-SO₃ molar ratios reported for this sorbent were calculated from the sulfur content of coal samples collected during the test, and an assumed 1% conversion of SO₂ to SO₃ as described above. The magnesium hydroxide content of the PHDL may be more reactive with flue gas SO₃ than the calcium hydroxide, so the Mg:SO₃ molar ratio might be a better metric for performance. The values in the paper for (Ca + Mg):SO₃ ratio can be divided by two to get the Mg:SO₃ mole ratio.

Also note that throughout this paper, SO₃ removal during slurry injection is reported as the percent reduction in SO₃ concentration measured at the ESP B outlet for injection versus baseline conditions. SO₃ removal percentages are only approximate, though, because there is some question as to what the uncontrolled concentrations might have been at any particular time. It was hoped that the ESP C outlet concentrations, which are on the side of the boiler not being injected, would provide a good source of uncontrolled concentrations. However, this did not turn out to be the case due to carryover of injected material to the west side of the boiler, which lowered the ESP C outlet values. Also, the coal sulfur content varied somewhat, ranging from 4.0 to 4.5%.

The first week of testing, SO₃ removal percentages were measured at 26% to 54%. An overnight, low-load, high injection rate test was conducted on October 26, and showed that only 47% removal was achieved (assuming a 25-26 ppm baseline) when injecting PHDL at a (Ca + Mg):SO₃ ratio of 8.2:1. This observed SO₃ removal was nowhere near the target value of 90% when injecting PHDL at the flow rate limit of the injection system, even at lower unit load. It was expected that SO₃ removal would improve with time, due to “boiler conditioning” with the buildup of alkali solids on heat transfer surfaces, but it was presumed that this effect would not improve SO₃ removal from less than 50% to over 90%. Consequently, it was decided to shut down and implement minor piping changes to increase the slurry injection rate capacity.

Overnight testing on November 1 represented a last attempt to achieve higher SO₃ removal percentages with the PHDL. The maximum slurry injection rate achievable was improved to about 20 gpm with the piping changes, but only for relatively short periods, as 20 gpm exceeded the ability of the air-driven slurry transfer pumps to maintain day tank level. A short-term test (about one hour) at a (Ca + Mg):SO₃ ratio of about 12:1 saw only about 35% SO₃ removal, based on an assumed baseline value of 25-26 ppm at the ESP B outlet. Although the test at this injection rate lasted only one hour, slurry injection had been running at a relatively high rate for about 12 hours prior to these measurements. Continued operation at a (Ca + Mg):SO₃ ratio of about 7:1 saw only about 25% SO₃ removal based on the assumed baseline value.

This overnight test also provided the first measurable evidence of solids crossover to the west side of the boiler under certain injection conditions. The ESP C outlet values were almost equal to those at the ESP B outlet, and appeared to track with the slurry injection rate.

Although the true baseline SO₃ concentrations for these low load tests are not known and the removal percentages are approximate, it is clear that PHDL slurry injection at the rates tested was not able to lower ESP B outlet SO₃ concentrations to the desired values of less than 5 ppm. It was decided to suspend PHDL testing. There were a few remaining issues associated with the PHDL tests, such as whether good slurry distribution into the boiler was being achieved and whether or not the furnace gas temperature was high enough at the 11th floor location to dead burn the reagent. However, since the SO₃ removal was generally 50% or less and the ESP B outlet SO₃ concentrations remained above 10 ppm, it was decided to test another reagent to see if higher percentages could be achieved.

Commercial Mg Test

For the second short-term slurry injection test, it was decided to test a commercially available magnesium hydroxide. Magnesium hydroxide and magnesium oxide have been widely used as fuel or furnace additives to control SO₃ formation in oil-fired applications, and to a lesser extent to control SO₃ in coal-fired applications. A literature review did not identify any previous application of magnesium hydroxide injection on a coal-fired boiler that achieved 90% SO₃ removal though, which is the target for this project.

The magnesium hydroxide tested is produced by Martin Marietta. This material is precipitated from magnesium chloride, which reportedly produces a finer particle size than the other common route to producing magnesium hydroxide – pressure slaking magnesium oxide. The precipitated material is produced as a 60 wt % aqueous slurry. The mass mean particle diameter is in the range of 5 to 6 microns, and the BET surface area is in the range of 15 to 16 m²/g. As was the PHDL, the viscosity and density of this material at 60 wt % solids was too high to be handled by the existing slurry injection system. Consequently, this material was diluted with plant service water as it was unloaded and injected at 30 wt %.

The commercial Mg test was conducted the first part of December 2000. The results of this test are illustrated in Figures 8 (week one) and 9 (week two). The Mg:SO₃ ratios shown in the figures are based on the magnesium hydroxide content of the slurry injected compared to one-half of the coal feed rate times the coal sulfur content, using the 1% factor for SO₂ to SO₃ conversion. Coal sulfur analyses for samples during this test averaged 4.0% sulfur.

Baseline SO₃ sampling was conducted on November 28, and commercial Mg injection began that afternoon. The baseline measurements showed a side to side SO₃ stratification at the ESP outlet that was not seen in the original baseline measurements in early October, showing only 19 ppm of SO₃ at the ESP B outlet and 30 ppm at the ESP C outlet (not shown in the figure). Immediately after injection began, at a Mg:SO₃ ratio of about 5:1, SO₃ measurements showed only about 10% SO₃ removal at the ESP B outlet. The next day, after almost 24 hours of slurry injection, the ESP B outlet SO₃ concentration dropped to 10-11 ppm, corresponding to a removal percentage between 40 and 45%.

Figure 8: Results from the first week of the commercial Mg test

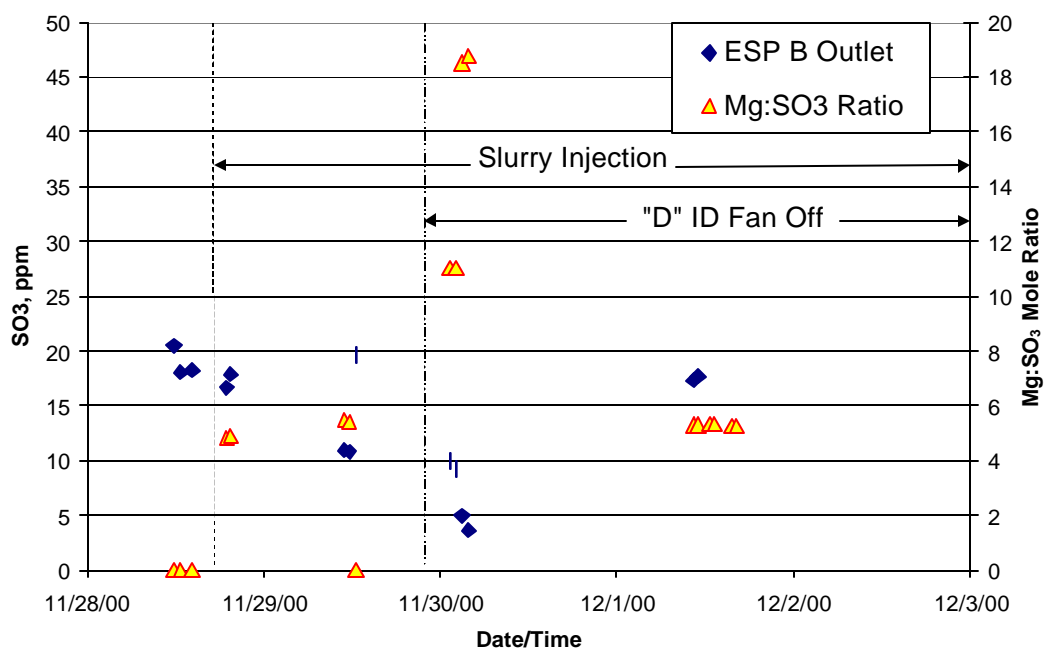
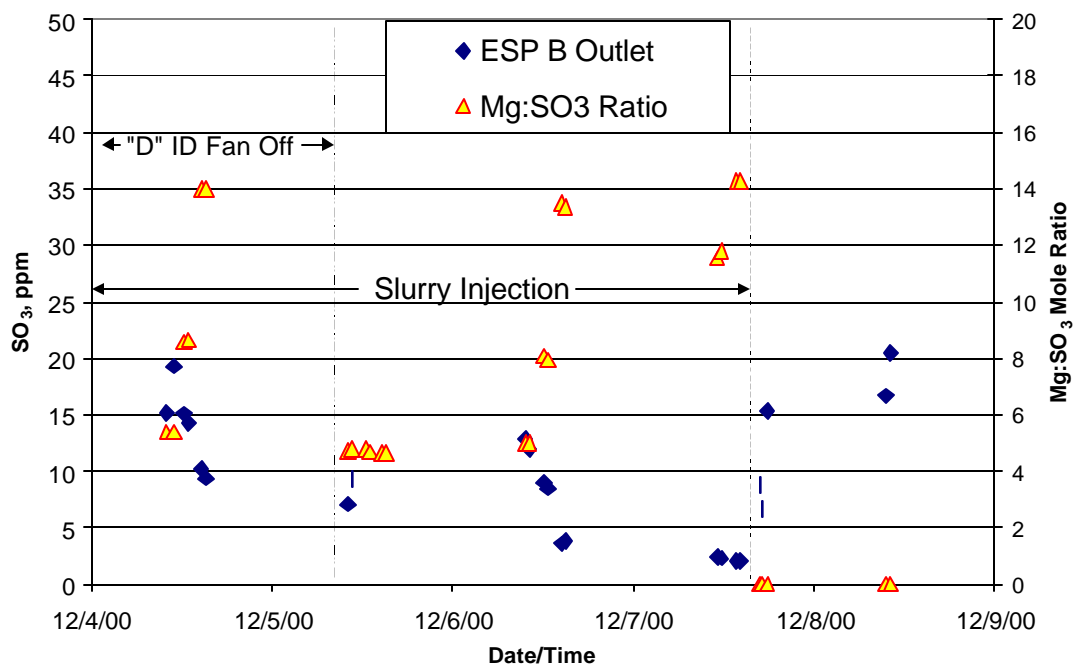


Figure 9: Results from the second week of the commercial Mg test



An overnight test was conducted November 30, with the unit load reduced to about 550 gross MW and increased injection rates. When injecting at a $\text{Mg}:\text{SO}_3$ molar ratio of 11:1, the ESP B outlet SO_3 was observed to drop below 10 ppm, representing about 50% removal. Injecting at a $\text{Mg}:\text{SO}_3$ ratio of almost 19:1, the ESP B outlet SO_3 concentration dropped below 5 ppm, representing 80 to 85% SO_3 removal.

This test on November 30 provided further evidence of sorbent migration to the west side of the boiler. The ESP C outlet SO_3 concentrations (not shown in the figure) dropped from the previous day's baseline value of 28 to 30 ppm to about 17 ppm at the 11:1 $\text{Mg}:\text{SO}_3$ ratio, and to about 12 ppm at the higher ratio. The "D" ID fan was out of service for this low load test. It was decided to conduct future testing with all four fans in service, to minimize side-to-side flue gas mixing that appeared to be caused by having one fan out of service (particularly "D").

By the last two days of operation, December 6 and 7, the commercial Mg sorbent had been injected continuously for over a week, at injection rates corresponding to about a 5:1 $\text{Mg}:\text{SO}_3$ ratio or better. It was expected that over that period the boiler would be "conditioned" by reaching a steady state buildup of MgO on heat transfer surfaces, and that SO_3 removal performance would continually improve with time. However, after a week of continuous injection it became apparent that the desired 90% SO_3 removal would not be achieved without increasing the injection rate above 5:1. From the afternoon of December 6 through the afternoon of December 7, the commercial Mg sorbent was injected at a $\text{Mg}:\text{SO}_3$ molar ratio of 12:1 to 14:1. After 24 hours of injecting at this rate, the ESP B outlet SO_3 concentrations were measured at 2.3 ppm for a 12:1 mole ratio, and 2.1 ppm at a 14:1 mole ratio. These values represent approximately 90% SO_3 removal, the target for this project.

On December 7 all four ID fans were in service. The apparent migration of sorbent over to the west side of the boiler was greatly reduced with all four fans in service, with the ESP C outlet SO_3 concentrations measured to be near baseline at 24 to 28 ppm.

The data from the evening of December 7 through December 8 show how rapidly SO_3 concentrations return to baseline levels after stopping sorbent injection. Within one to two hours of stopping injection, the ESP B outlet SO_3 concentrations increased to a level corresponding with about 55 to 65% removal, and by the next morning had returned to baseline values.

Byproduct Mg Test

The third short-term slurry injection test was conducted mid-February, 2001, using byproduct magnesium hydroxide produced at Allegheny Energy's Pleasants Station. The Pleasants Station has a Dravo ThioSorbic[®] Lime FGD process that employs magnesium-enhanced lime scrubbing with ex situ forced oxidation to produce a gypsum byproduct. The remaining liquor after the gypsum is recovered is further processed by lime addition to precipitate a mixture of magnesium hydroxide and gypsum particles. This stream is purified to recover most of the gypsum, and a second byproduct is a slurry that contains a mixture of magnesium hydroxide (about 60% of the solids) and gypsum fines (most of the remainder). With the equipment configuration at Pleasants Station, the byproduct slurry is produced at about 15 to 20 wt % total suspended solids. For the short-term byproduct Mg slurry injection test, the byproduct slurry was trucked from Pleasants

Station and unloaded into the storage tanks at BMP Unit 3. Several truckloads per day were required at the slurry injection rates tested. The solids in this slurry average about 4 to 5 microns for a mass mean particle diameter, and have a specific surface area of about 49 to 63 m²/g.

The results from the byproduct Mg test are summarized in Figures 10 (first week) and 11 (second week). Mg:SO₃ molar ratios in the figures are based on the amount of Mg in the byproduct slurry, one-half the Unit 3 coal feed rate, and ultimate analyses of coal samples for the test period. The coal quality was quite variable during the test period, and coal sample sulfur levels were lower than during the previous tests, averaging about 3.5 wt % for this test versus about 4% for previous tests. In spite of the coal analyses showing lower sulfur content, the baseline SO₃ concentrations measured on February 13 were as high as previous measurements with the higher-sulfur coals. Given that normal baseline SO₃ concentrations were seen, the Mg:SO₃ ratios shown in the figure may be biased high by 10-15% because of the lower coal sulfur values used in the calculations.

Most of the baseline samples were taken with either the “A” or “C” ID fan out of service. Since the ID fans in service affect the flow rates through the air heaters, they can also affect downstream SO₃ concentrations. This may explain why the baseline values for the ESP B outlet were initially higher than they had been for the commercial Mg test.

Unit 3 operated on three ID fans (“A” out of service) most of the first week. Testing was conducted at Mg:SO₃ molar ratios of about 6:1, and ESP B outlet SO₃ concentrations were typically about 10-12 ppm. This represents about 40-50% SO₃ removal based on a 20 ppm baseline value, 60-70% removal if the baseline values were actually 30 ppm as measured earlier in the week.

Figure 10: Results from the first week of the byproduct Mg test (11th floor injection)

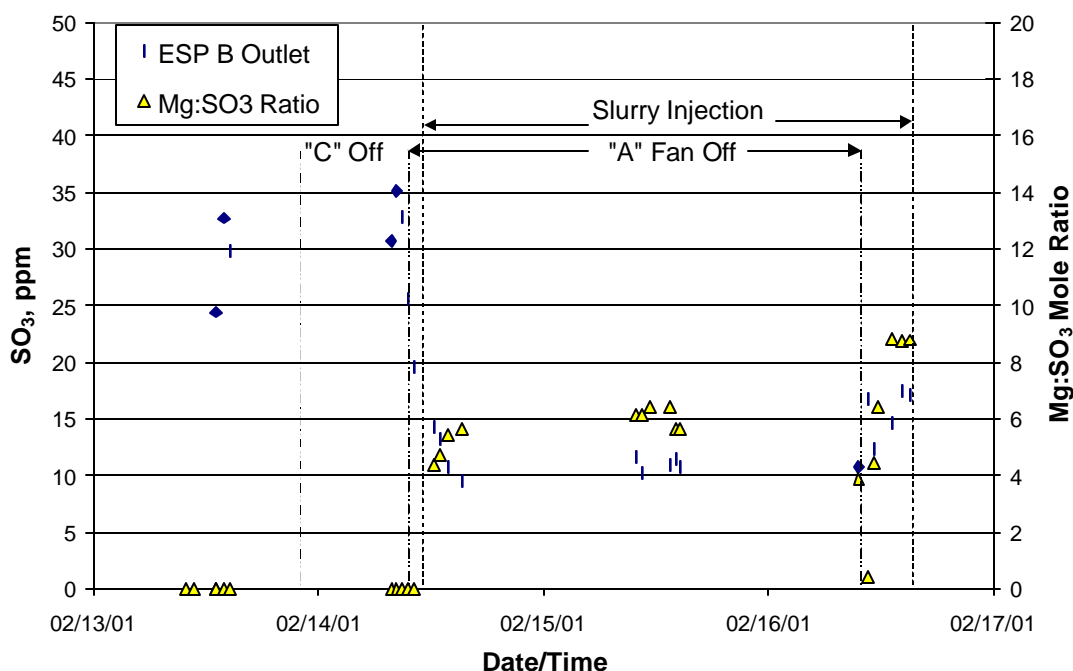
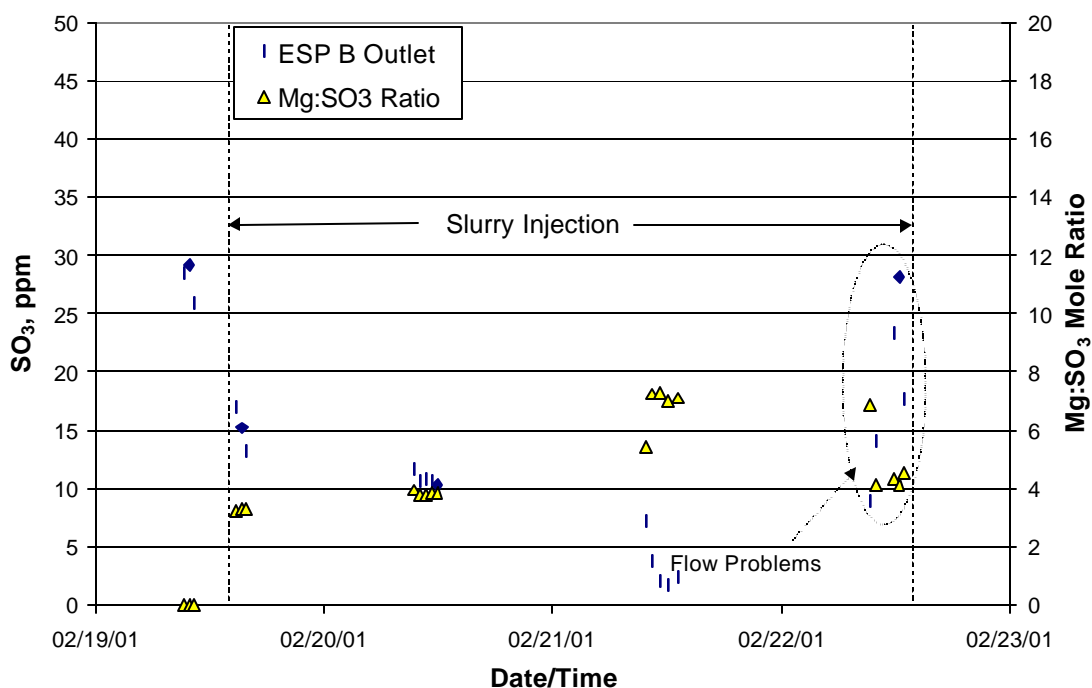


Figure 11: Results from the second week of the byproduct Mg test (14th floor injection)



Late on February 16, the slurry injection rate was raised to the maximum pumping capacity, corresponding to a Mg:SO₃ molar ratio of almost 9:1. Midway through the afternoon, the “A” ID fan was put back in service, meaning all four ID fans were operating. The ESP B outlet SO₃ concentrations measured at this high injection rate were high, ranging from 15 to 17 ppm.

Because it had not been possible to lower the ESP B outlet SO₃ concentrations below 5 ppm as desired, it was decided to move the injection location higher in the furnace, to the 14th floor of the boiler structure. There was concern that furnace gas temperatures were too high at the 11th floor location, causing the sorbent to dead burn. The injection system was shut down while the injection system was repositioned, and testing resumed on February 19.

Unit 3 operated with all four ID fans in service the entire second week of testing. Baseline SO₃ concentrations at the ESP B outlet were relatively high, averaging 28 ppm. Injection began the afternoon of February 19, at a Mg:SO₃ molar ratio of about 3:1, and by late in the afternoon the ESP B outlet SO₃ concentration was down to 13 ppm, representing over 50% removal. Injection continued the next day at a rate corresponding to a Mg:SO₃ ratio of 4:1, and ESP B outlet SO₃ concentrations dropped to about 10-11 ppm, representing just over 60% SO₃ removal.

However, the target was to lower the ESP B outlet SO₃ concentration below 5 ppm, so overnight the injection rate was increased to a Mg:SO₃ molar ratio of about 5:1 to 6:1. The first measurement on February 21 showed the ESP B outlet had dropped to 7 ppm, representing over 70% removal. A further increase in injection rate during the day, to a Mg:SO₃ ratio of about 7:1, lowered the ESP B outlet SO₃ concentration to an average of 2 ppm, which represents over 90%

SO₃ removal compared to the baseline values on February 19. The ESP C outlet (not shown in the figure) showed evidence of sorbent crossover to the west side of the furnace when injecting at this higher rate, dropping from about 35 ppm the day before to about 20-25 ppm when injecting at a 7:1 Mg:SO₃ ratio.

It was desired to continue injecting at an intermediate rate between a 4:1 and 7:1 Mg:SO₃ molar ratio overnight. Since the end of the byproduct Mg test was scheduled for the next day, the 10,000-gallon storage tanks were being depleted of inventory. Although the injection system ran smoothly overnight, as the tank inventories began to deplete the morning of February 22, the injection rate became unstable due to continued pump suction line plugging. As a result of the intermittent injection on February 22, the ESP B outlet SO₃ concentrations were much higher than were expected based on the results of the previous day. Also, the ESP C outlet data from February 22 (not shown in the figure) suggest a higher than normal baseline SO₃ for that day, with an average of almost 40 ppm.

The objective of the project of achieving greater than 90% SO₃ removal, as measured at the ESP B outlet location, was achieved with the byproduct Mg slurry after the injection location was raised to the 14th floor elevation. Due to the slurry flow problems on February 22, it was not possible to get more information about removal versus injection rate for a “conditioned” boiler.

Balance of Plant Effects

Balance of plant effects were focused on the impacts on ESP performance during the short-term slurry injection tests. There were two concerns about sorbent injection impacts. One was that the injected material itself (which typically represented less than 5% of the particulate loading to the ESP's) would be difficult to collect, and the other was that removal of SO₃ from the flue gas upstream of the ESP would adversely affect the fly ash resistivity. The impacts of sorbent injection were typically measured by recording ESP electrical operating conditions (secondary current and voltage) for each electrical section several times each test, and by reviewing the outputs from the unit's ESP outlet opacity monitors.

PHDL Injection Test

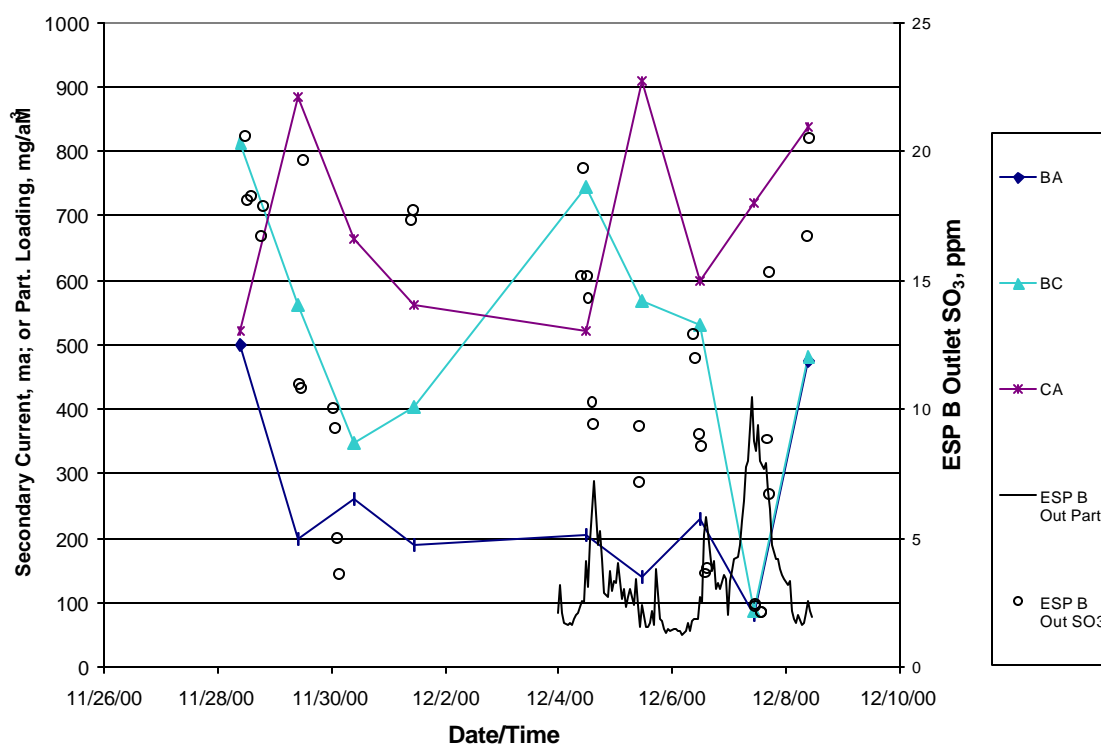
The PHDL injection test saw slurry injection rates up to 20 gpm at 35 wt % solids, but never high SO₃ removal percentages. The lowest SO₃ concentration measured at the ESP B outlet was greater than 10 ppm, which should be adequate for fly ash conditioning. The ESP B inlet concentrations were even higher, so no effect of SO₃ removal on fly ash resistivity was expected. The secondary current values for all four electrical fields of ESP B showed no effect of sorbent injection. It was concluded that the PHDL itself did not measurably affect the ESP electrical conditions, nor did the moderate SO₃ removal achieved with this sorbent.

Commercial Mg Injection Test

Commercial Mg was the first slurry that achieved 90% SO₃ removal, lowering the ESP B outlet SO₃ concentrations to 2 ppm and inlet concentrations to 2-3 ppm. Figure 11 illustrates secondary current values for all four electrical sections of ESP B, and for the first section of ESP C during

the test period. Also shown are the ESP B outlet SO_3 concentrations and the ESP B outlet particulate loading as indicated by the plant's opacity monitor (second week of the test only). The data show an immediate drop in the secondary current in the first field of ESP B when sorbent injection began, from about 500 Ma to 200-250 Ma. Effects on the downstream fields were not as consistent, with some fields increasing and some decreasing after sorbent injection began. We would expect initial effects of sorbent injection to be most pronounced for the first field of the B ESP, though, most likely due to a space charge effect from the additional small particles added to the flue gas by the sorbent.

Figure 11: Effects of commercial Mg injection on ESP secondary currents and particulate emissions



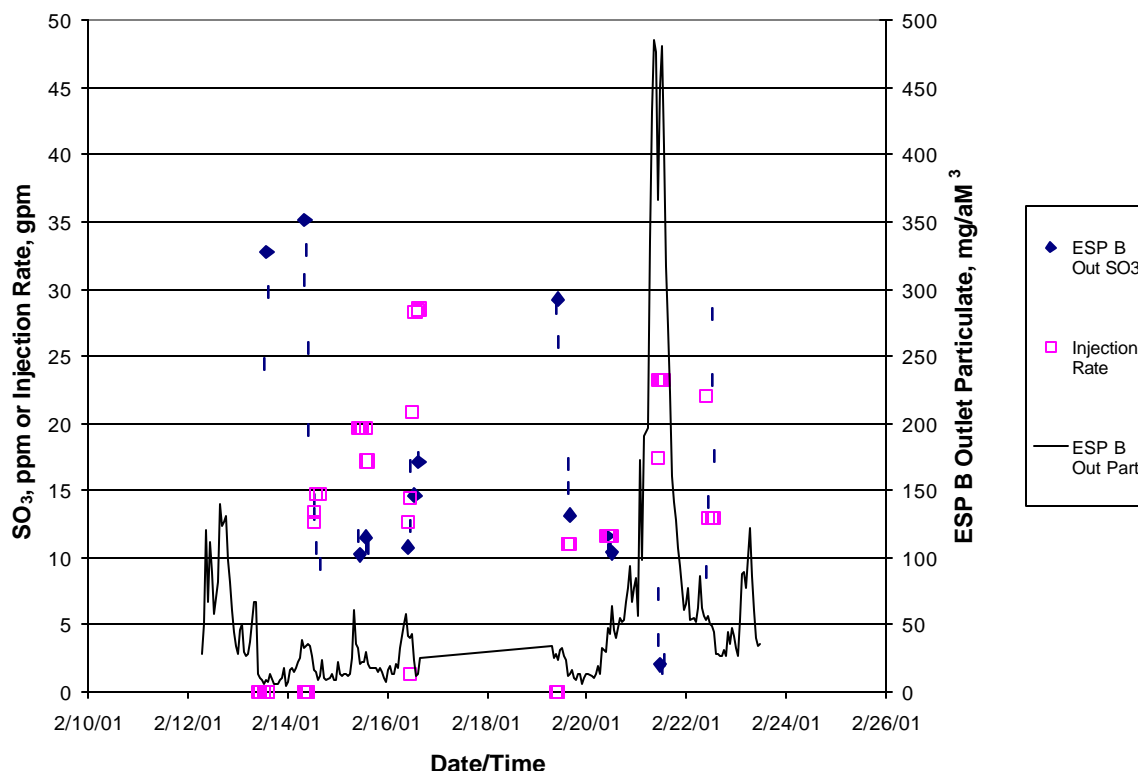
The most pronounced effect is seen December 7, when the sorbent injection rate was high and the ESP B outlet SO_3 was lowered to 2 ppm. ESP operating conditions show that secondary current values for all four electrical sections were reduced below 100 Ma. Similarly, the power input to those electrical sections (not shown in the figure) was lowered to about 3 kW during this period, as opposed to normal input values of 20 to 40 kW. The ESP B outlet opacity showed a dramatic increase in mass loading at the ESP B outlet during this same time period. The ESP electrical condition and outlet emission impacts appear to be directly related to sorbent injection and/or SO_3 removal, as values returned to normal the next day, after sorbent injection stopped.

Byproduct Mg Injection Test

The byproduct Mg test also achieved approximately 90% SO_3 removal as measured at the ESP B outlet. ESP B inlet SO_3 concentrations were lowered to 3-4 ppm, and outlet concentrations to 2

ppm. Due to technical difficulties, ESP operating current and voltage values were not recorded for this test. Therefore ESP outlet particulate loading as indicated by the plant's opacity monitor are the only available data about the effects of byproduct Mg injection on ESP operation. These data are summarized in Figure 12.

Figure 12: Effects of byproduct Mg injection on ESP B particulate emissions



The most pronounced effect was seen overnight February 20 and during the day February 21, when the sorbent injection rate was high and the ESP B outlet SO₃ concentration was lowered to 2 ppm. The ESP B outlet opacity showed a dramatic increase during this time period. The adverse effect appeared to be directly related to the effects of high SO₃ removal, as values from the next day returned to normal after sorbent injection rates were reduced and the ESP B outlet SO₃ concentrations increased to 9 ppm and greater. Also, the adverse effect did not appear to be related to sorbent injection rate per se, as a higher injection rate was previously experienced on February 16, with no apparent effect on ESP performance. The February 16 data were for slurry injection at the 11th rather than 14th floor, and high SO₃ removal efficiencies were not achieved.

SUMMARY AND CONCLUSIONS

Three of the four sorbents tested were able to achieve the target of 90% SO₃ removal as measured upstream of the FGD system. The sorbent that did not, PHDL, may have been adversely affected by the higher furnace temperature at the 11th floor level at which it was injected. The most cost effective sorbents for First Energy's application appear to be dolomite injected through the burners and byproduct Mg injected into the upper furnace. Dolomite injection through the burners appears to be particularly suited for plants with lime-based scrubbers for combined particulate

and SO₂ removal, as the excess dolomite can offset lime consumption in the FGD system. First Energy is further testing this option on Units 1 and 2 at BMP, outside the current project.

Byproduct Mg injection appears to be the more attractive option for plants with a more common emissions control configuration, with an ESP followed by an FGD system. This sorbent will be tested in a 25-day longer-term test on BMP Unit 3, starting in mid-May 2001. The longer-term test will quantify how much byproduct Mg must be injected to achieve high SO₃ removal across the entire furnace, and to determine balance of plant effects such as on slagging, ESP performance, and removal of HCl, HF and arsenic from the flue gas. Based on short-term test results, ESP impacts will be of particular interest. Effects of sorbent injection on SCR catalyst coupons will also be evaluated over the duration of the test.

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